

# PATENT SPECIFICATION

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## (54) PRECONDITIONER FOR METALLIZING OF POLYOLEFINS

- (71) We, AVISUN CORPORATION, a corporation organised under the laws of the State of Delaware of 21 South Twelfth Street, Philadelphia, Pennsylvania 19107, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a process for metallizing moulded polyolefin articles, especially those made of polypropylene.
- More particularly, this invention relates to a method of treating the surface of polyolefin articles to render them more easily amenable to deposition of metallic coating thereon, for example by electroplating or vacuum metallizing. Still more particularly, this invention relates to the substantial elimination of surface strains in moulded polypropylene articles which cause problems in subsequent deposition of metallic coatings.
- The problem of causing ink, paint, or other types of coating to adhere to the non-polar surface of polyolefins is well known. In general, an approach to solving the problem has been to modify the surface of the polyolefin by surface oxidation to introduce polar groups onto the surface. For example, in the case of electroplating, one may treat the poly olefin article with a strong mineral acid containing chromium trioxide or an alkali metal chromate. The mineral acid used should be a strong one capable of oxidizing the polyolefin surface. Concentrated sulphuric acid, phosphoric acid, or mixtures thereof have been used with high degrees of success. The purpose of this treatment is to induce surface oxidation. After the acid treatment, the surface of the article is sensitized with a solution of a readily oxidizable salt such as stannous chloride. The polyolefin article is then treated with an aqueous solution of a noble metal salt (for example, palladium chloride) which is reduced by the oxidizable salt present on the surface. This forms a metallic film at discrete activated sites. The activated material is then subjected to electroless plating using copper, nickel or cobalt as the metal. This may be accomplished by immersing the treated surface in a metal salt solution which also contains a reducing agent such as formaldehyde or trioxymethylene. Sufficient metal is thereby deposited on the surface to form a continuous metallic film capable of conducting electricity. The polyolefin article may then be conventionally electroplated with copper, followed by nickel or chromium, or just with nickel followed by chromium. The thickness of the metal coatings is generally within the range of about 0.1 to 1.5 mils. In this method it is desirable to rinse the surface with water following each of the above-mentioned steps.
- The electroplating of polyolefin articles with a metal plate having a thickness in the range of about 0.1 to 1.5 mils in such a way that the plate is tightly bonded to the polyolefin substrate constitutes a highly desirable goal. This is especially true in view of recently developed polyolefins which are considered engineering plastics and which may be used as substitutes for various materials of construction. An electroplated metal coating having good adhesion to the plastic substrate improves the structural properties of the plastic, such as resistance to deformation, thereby enhancing its use as a substitute for metals. The advantages of using polyolefins in such applications include lower cost of materials, cheaper tooling and tool maintenance, lower finishing costs in buffing and polishing, and lower shipping costs. The use of polyolefins, furthermore, allows greater versatility of product design and gives a more corrosion-resistant end product. Good adhesion between the metal plate and the polyolefin substrate causes improvement in physical properties such as flexural modulus, impact strength, and temperature deflection.
- Another method of applying a metallic coating to a nonconductive polyolefin article is vacuum metallizing. This well known and conventional procedure involves the principle of evaporation of metals under high vacuum.

[Price 25p]

Representative of typical metals that may be applied using this technique include aluminum, copper, and silver. Generally, vacuum metallizing involves the steps of (a) applying a suitable undercoat or prime coat to the polyolefin article, (b) evaporating the desired metal under high vacuum, and (c) applying a topcoat lacquer to protect the thin metallic deposit. Suitable undercoats that are applied to the polyolefin article are well known and are generally a dispersion or solution of an acid containing polymer such as carboxylated butadiene polymers, and maleic anhydride modified atactic polypropylene polymers. As the topcoat, any commercially available thermosetting acrylic lacquer may be used.

It is well known that when moulding polyolefin articles, especially into complex shapes, strains occur within the material and these strains cause poor results when applying metallic coatings to the polyolefin material. Therefore, it is desirable to eliminate these strains prior to depositing metallic coatings upon the moulded surfaces. It is an object of this invention to improve the quality of metallic coatings applied to moulded polyolefin articles. Another object of this invention is to prepare the polyolefin material for surface conditioning or etching prior to plating the surface with metals. A further object of this invention is to relieve the strains in the polyolefin produced by the moulding procedure, prior to conditioning the polyolefin for electrodeposition of a metal coating. Specifically, the object of this invention is to precondition articles formed from commercially available polyolefins and in particular polypropylene, in order to render them metallizable by standard means applicable to the commercial plating of other plastics.

We have found that the foregoing objects may be obtained by contacting the article to be plated in accordance with the above-described procedure with certain ketones at a temperature of from 20°C. to the boiling point of the ketone for a period of from 1 minute to about 15 minutes prior to oxidizing the polyolefin surface or treating the surface with a primer coating. Higher temperatures enable reduced contact time and therefore the time may be less than one minute. Contact time in excess of 15 minutes is not considered practical. Preferred ketones to be used with this invention have a boiling point less than 140°C., should be at least slightly soluble in water or dispersible or emulsifiable in water, and should be capable of penetrating the surface of the polyolefin article. Ketones having these properties include acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone and ethyl t-butyl ketone. The ketone may be at least partially removed from the surface of the polyolefin

article by washing with water prior to the mineral acid treatment. The contacting of the article with the ketone may take place either in the liquid or vapour state of the ketone. Methyl ethyl ketone and acetone are particularly suitable for pretreating articles which have been moulded from polypropylene.

After such pretreatment the polyolefin, if electroplating is contemplated, is conditioned by treatment with (1) a strong mineral acid containing chromium trioxide or an alkali metal chromate, (2) a solution of a tin salt, (3) a solution of a noble metal salt, and (4) a solution of a reducible salt of nickel or copper. The polyolefin is then electro-plated with a metal film in accordance with conventional practice.

Alternatively, the polyolefin may be vacuum metallized by any known technique.

At this time, we are not certain as to the mechanism by which the pretreatment step of this invention improves the bond strength of the electroplated coating. At least two theories have been advanced to explain the surprising improvements obtained. One theory is that the material is stressed when moulded and pretreatment in accordance with this invention relieves the stresses which cause poor metallizing characteristics. This would be by a type of local or surface annealing action. The other theory is that the pretreatment causes the moulded material to be more easily attacked by the mineral acid used in the conditioning step of the electroplating process. This permits better oxidation of the surface and the formation of polar groups for receiving the metal ions during the electroplating.

In order to demonstrate the benefits obtained by treating polyolefins according to the method described in this invention, a series of experiments were performed. The bond strength of the electroplate to the substrate was measured by a standard pull test. In this test, two parallel cuts are made in the metal about 1/2-inch apart. An additional vertical cut is made between the two parallel cuts to form a tab and one end of the resulting tab is raised sufficiently to allow gripping by a tensile testing machine. The specimen is then placed in a tensile tester and the tab is pulled vertically from the surface of the polypropylene. The force required to pull the tab is measured as the bond strength.

The polyolefins treated according to this invention are polymers prepared from the monomeric olefins, having from 2 to 8 carbon atoms. Such polyolefins, therefore, include polyethylene, polypropylene, ethylene-propylene copolymers, ethylene-butene-1 copolymers, polybutene-1, poly(4-methyl-pentene-1), poly(3-methylbutene-1), and the like. The term polyolefin as used herein is, furthermore, intended to include

5 copolymers of the above defined olefinic monomers with functional olefinic monomers in which such functional olefinic monomers constitute a minor proportion by weight of the copolymer. The term "functional olefinic monomers" is intended to mean monomers which contain, in addition to the olefinic double bond, functional groups such as nitriles, ethers, carboxylic esters and alcohols. Functional olefinic monomers frequently employed in combination with the olefinic monomer are in particular the acrylic monomers such as methyl methacrylic, ethyl acrylate, and acrylonitrile and the vinyl esters such as vinyl acetate. The polyolefins can contain inert inorganic fillers such as asbestos fibers, glass fibers, carbon, silica, talc and alkaline earth salts which are frequently added to improve the rigidity of the polyolefin. In addition, the polyolefins can contain other additives normally added to the polyolefin in order to improve fabricability or solid state properties of such polyolefin.

#### Example 1

25 A plaque 5" X 5" X 110 mil of crystalline polypropylene having a flow rate of 5.0 (ASTM D - 1238 - 62T) was electroplated in accordance with the method described above but without the use of the pretreatment which is disclosed and claimed herein. The polyolefin plaque was moulded from a homopolymer polypropylene considered to be a general purpose type. The resulting electroplate had zero bond strength. Four other plaques moulded from the same crystalline polypropylene were pretreated by placing the plaques in a bath containing methyl ethyl ketone at a temperature of about 78°C. for various periods of time. After such pretreatment, the plaques were electroplated according to the method described above and it was found that the bond strengths were significantly improved.

The results from this experiment and the ones following are presented in the table below. 45

#### Example 2

The procedure of Example 1 was repeated but this time the pretreatment was performed using acetone at 50°C. rather than methyl ethyl ketone. Again, the bond strength greatly increased. 50

#### Example 3

The procedure of Example 1 was repeated using propylene-ethylene copolymer (flow rate 4.0) plaques instead of homopolymerized polypropylene plaques. After plating in accordance with the method described above it was found that the electroplate blistered from the untreated plaque but that the treated plaques had relatively high bond strengths. 55 60

#### Example 4

Crystalline polypropylene having a flow rate of about 4 and modified by the addition of 0.5 part by weight of "Triton" X-100 (The word "Triton" is a Registered Trade Mark), a commercially available nonionic surfactant of t-octylphenoxy-polyethoxyethanol, 0.5 part of dilauryl thiodipropionate a 5 parts of TiO<sub>2</sub> was moulded into 2" X 5" X 110 mil plaques and treated in accordance with the procedure outlined in Example 1. In this case, the pretreatment time was varied as was the temperature at which the methyl ethyl ketone was maintained. Even without pretreatment, the modified polypropylene plaques moulded from the modified polypropylene electroplatable formulation accepted the electroplate and had a fairly good bond strength. However, after pretreatment, it was found that there was some additional increase in bond strength. 65 70 75 80

TABLE

Example	Pretreatment Solvent	Solvent Temp., °C.	Bond Strength (lbs./linear inch)				
			Pretreatment Time (minutes)				
			0	1	2	3	5
1	None	—	0				
	MEK	78		34	25	36	36
2	None	—	0				
	Acetone	50		18	17		
3	None	—	0				
	MEK	78		24	25	22	22
4	None	—	20				
	MEK	78		28	29	23	28
	MEK	50		21	21	34	16
	MEK	25		23	20	21	25

## WHAT WE CLAIM IS:—

1. A process for the deposition of metallic coatings on a shaped polyolefin as hereinbefore defined article, comprising pretreating the shaped article by contacting the article with a ketone which is dispersible, emulsifiable or at least slightly soluble in water, the extent of the contacting being such that the ketone penetrates the surface of the polyolefin article and thereby relieves strains in the surface of the polyolefin article and then depositing the metallic coating on the shaped article.
2. A process as claimed in Claim 1 wherein the deposition of metallic coatings is accomplished by electroplating or vacuum metallizing the shaped polyolefin article.
3. A process as claimed in claim 1 or 2 wherein the polyolefin is polypropylene.
4. A process as claimed in any of claims 1 to 3 wherein the ketone is acetone or methyl ethyl ketone.
5. A process as claimed in any of claims 1 to 4 wherein the contacting is performed with a ketone in a liquid state.
6. A process as claimed in any of claims 1 to 4 wherein the contacting is performed with a ketone in the vapour state.
7. A process as claimed in Claim 1 wherein the pretreating is accomplished by contacting the shaped polyolefin article with a ketone having a boiling point of less than 140°C. for a period of from one minute to fifteen minutes and at a temperature of from 20°C. to the temperature at which the ketone boils, and thereafter washing the article prior to treating it with a metallizing process.
8. A process as claimed in Claim 7 wherein the metallizing process is electroplating.
9. A process as claimed in Claim 8 wherein the pretreated polyolefin article is subsequently treated with
  - (2) a strong mineral acid solution containing chromium trioxide or an alkali metal chromate;
  - (b) a solution of tin salt;
  - (c) a solution of a noble metal salt; and
  - (d) a solution of a reducible salt of a metal selected from the group consisting of nickel and copper;
 is then electroplated to deposit a film of metal on the surface of the shaped polyolefin article.
10. A process as claimed in Claim 7 wherein the polyolefin is polypropylene and the ketone is acetone.

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